

A Dynamic Pathway for Stone-Wales Bond Rotation on Carbon Nanotube through Diamond-like Bonds

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Abstract

A new lower energy barrier with a two-step pathway of Stone-Wales (SW) bond rotation on carbon nanotubes (CNTs) is found through molecular dynamics (MD) simulations of CNTs under tension. The first step involves going over to a stable sp^3 -like metastable configuration with half rotated and partially tilted C-C bond. The second step involves going over to the fully rotated C-C bond with the formation of a SW defect in the nanotube. The energy barrier for this two-step *dynamic* pathway is significantly lower than the previously known *static* barrier for in-plane rotation of the C-C bond on a tensile strained ($> 4\%$) CNT.

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The atomic structure of carbon nanotubes [1, 2] is ideally composed of perfect hexagons, though several types of defects can form on the surface such as dislocations, diamond-like bond defects, vacancies or adatoms. The Stone-Wales (SW) bond rotation is one of the defects that has been widely proposed for the indirect in-plane exchange of atoms on graphite layers [3]. A SW bond rotation involves rotating a nearest neighbor C-C bond by 90 degree on a graphite plane, resulting in the formation of pentagon-heptagon defect pairs in such a way that the characteristics of sp^2 bonds is maintained in the final structure. SW bond rotation defects were first investigated for the study of self-diffusion in graphite planes [4]. Since the discovery of CNTs, there have been many theoretical studies on the formation of SW rotation defects on CNTs using various methods [2, 5–8] for two reasons. First, the pentagon-heptagon defect pairs from SW rotation are used in creating CNT heterojunctions for electronics applications [9–13]. Second, more recently the SW bond rotation defects have been proposed to play essential roles in the yielding of CNTs under tensile strains [5–8, 14, 15].

The formation of a SW bond rotation defect on a CNT under *static* conditions at zero strain has to overcome an activation barrier of about 7-8 eV with a positive formation energy of about 3-4 eV [6, 8]. When an external tensile stress is applied, both the activation barrier and the formation energy of SW defects decrease as the energy to break a C-C bond on a tensile stressed CNT is smaller than on a non-strained CNT. The transformation from the initial sp^2 configuration of all hexagon to the final sp^2 configuration of a pentagon-heptagon pair defect under *static* conditions is smooth and goes over a single activation barrier for in-plane bond rotation. Recently we have performed extensive finite temperature molecular dynamics (MD) simulations on CNTs under tensile strain close to their yielding point [14, 15]. A new SW bond rotation pathway is found in these dynamics simulations. We show that this new *dynamic* pathway involves a two-step process with an intermediate metastable state at a saddle point where sp^3 -like bonding configuration is observed and the activation barrier is lowered as compared with pathways of direct in-plane sp^2 - sp^2 type transformations.

The MD simulations use Tersoff-Brenner potentials [18, 19] for C-C interactions, which are parameterized from structures of diamond, graphite and small hydrocarbon molecular systems. Recently, Tersoff-Brenner potential has been used extensively to study the mechanical properties of CNTs, and gives results comparable to other more accurate methods,

such as tight binding [6, 7] or density functional theory [8] based methods. Details of MD simulations of tensile straining and yielding of CNTs as a function of strain rate and temperature have been reported recently, in which the yielding of CNTs is found to be triggered by SW bond rotation defects [14, 15]. The yield strain is found to be strongly dependent on the activation energy of SW bond rotation defect, and also has a logarithm dependence on strain rate and linear dependence on $1/T$ [14].

A 6nm long CNT (10,0) is tensile strained at 13.75% with its end atoms fixed and other atoms dynamically relaxed. A sequence of configurations of the 13.75% tensile strained CNT (10,0) during the MD simulation at $T = 800$ K is shown in Fig. 1a. The temperature is controlled by the Langevin friction force scheme [20], and in Fig. 1a we show a section of the CNT on which a typical SW bond rotation is observed. It can be seen that an intermediate state with sp^3 -like bond structure occurs at a rotation angle of about 30 degree between the initial and final state. With the continuing rotation of the C-C bond, the final structure of the pentagon-heptagon defect pair formation is obtained at the end. These four configurations are taken directly from MD simulations. For comparison, an illustration of a pathway of direct in-plane (sp^2 - sp^2 type) bond rotation without any intermediate state is shown in Fig. 1b. We slowly cooled the intermediate configuration (labeled as “2” in Fig. 1a) from the initial 800K to near 0K and found that such structure is in a local energy minimum. The fully relaxed and stable structure is shown in Fig. 1c, in which the rotated C-C bond is tilted away from the CNT surface. Similar intermediate states of the SW bond rotation, with formation of sp^3 -like bonds, were also observed on other tensile strained nanotubes such as (5,5) CNT in MD simulations. We focus on the energetics of this “new” *dynamic* pathway of SW bond rotation on the (10,0) CNT.

The change in the strain energy of the 13.75% tensile strained CNT (10,0) as a function of the C-C bond rotation angle during the MD process is plotted in Fig. 2. Data points labeled 1-4 in Fig. 2 are for the corresponding configurations shown in Fig. 1a. The energy of the quenched (from 800K to 0K) structures of these four configurations is marked as hollow squares in Fig 2. It can be seen that the intermediate sp^3 -like bonding state is at a saddle point and the SW bond rotation involves overcoming of two back-to-back barriers. This suggests that the energy lowered by forming the sp^3 -like bond in the intermediate state compensates for the local strain-induced energy. For comparison, the strain energy changes during direct in-plane SW bond rotation at strains of 0% and 13.75% are also shown in Fig.

2. It is not surprising to see that the activation barrier of SW bond rotation and also the formation energy are lowered with applied tensile strain, as in agreement with the previous studies [5, 8]. The more important feature, however is that the “new” pathway from the dynamic MD simulations has substantially lowered the activation barrier to about 1.2 eV as compared to the *static* barrier of about 3.5 eV under the same applied tensile strain. The new pathway with an intermediate saddle point goes through a two-step activation process, and the overall barrier is effectively lowered.

The extent of this new pathway as a function of strain is investigated systematically by slowly cooling (from 800K to 0K) and gradually changing the external strain on the 13.75% tensile strained (10,0) CNT at the saddle point. The thus obtained configuration remains the local energy minimum at the saddle point, with the sp^3 -like structure remaining intact at the defect site. Starting from this local energy minimum configuration, the C-C bond is rotated backward to the initial undefected structure and forward to the final defected structure with a pentagon-heptagon pair. The above process is repeated at many strain values. The change in the bond rotation energy of the CNT as a function of the rotation angle at various tensile strain between 0% to 18% is plotted in Fig. 3. It can be seen that, for small strain ($< 4\%$), there is no obvious intermediate metastable state and the activation barrier is about 8 eV. This is similar to that from the calculation of direct pathway by in-plane rotation of the C-C bond [5, 8]. The *dynamic* pathway starts to differ from the in-plane rotation pathway at higher strains. For tensile strains equal to and larger than 4%, the intermediate metastable state begins to appear and is stabilized at about 30 degree of rotation angle (which decreases slightly at larger strain values), resulting in the formation of a two-step or double-peak pathway. The activation energy as a function of tensile strain is plotted as insert in Fig. 3. The solid line with circles is for the activation barrier for the first step, while the solid line with triangles is for the activation barrier for the second step. It is noted, therefore, that the first barrier is the dominant one at all strains studied ($< 18\%$) and can be viewed as the effective activation energy. For comparison, the activation energy for a *static* in-plane C-C bond rotation (the one shown in Fig. 1b) is plotted as dashed line in the insert. For small strains ($< 4\%$), the activation barriers for the two pathways are similar. For strains equal to and larger than 4%, the double-peak pathway provides a lower energy barrier. For very large strain ($> 18\%$), there is a drop of activation energy for the direct in-plane bond rotation pathway.

A more accurate quantum generalized tight binding molecular dynamics (GTBMD) method of Menon and Subbaswamy[21] is used to investigate and confirm the intermediate state at the saddle point with the sp^3 -like bonds. The structure of a 12% tensile strained (10,0) CNT at the saddle point from Tersoff-Brenner potential was further relaxed with the GTBMD method. The intermediate saddle point structure is found to be local energy minimum configuration in the GTBMD method as well. While the main feature of the sp^3 -like bond structures is found to be similar to the one shown in Fig. 1c, the further relaxed structure from the GTBMD method shows more characteristics of sp^3 -like bonding with a larger tilting of the rotated C-C bond in the direction perpendicular to the CNT surface plane. For the 12% strained (10,0) CNT, a detailed search of pathway by varying the rotation angle and tilting distance of the C-C bond was conducted using the GTBMD method. Starting from the intermediate stable structure, a search along both the forward and backward rotation directions was carried out. The double-peak pathway with a stable sp^3 -like bonding configuration at the saddle point is verified and shown in Fig. 4. The effective energy barrier at 12% strain is found to be 2.5 eV, which is about half of the 5 eV activation barrier obtained using the direct in-plane bond rotation pathway at the same tensile strain using the GTBMD method. At the 12% tensile strain, the activation barrier (2.5 eV) for the double-peak pathway by the GTBMD is higher than that (1.3 eV) from Tersoff-Brenner potential on the same pathway. More simulations using the GTBMD method at other tensile strain values could be helpful, but are prohibitively expensive for an extensive search at the present.

In summary a new pathway of SW bond rotation through an intermediate saddle point state, with sp^3 -like bonds, is found through MD simulations. Calculations (with Tersoff-Brenner potential) on the energy barrier at 4 – 18% tensile strained CNTs show that at large tensile strain the new pathway has significantly lower activation energy, as compared with the one through the direct in-plane bond rotation pathway without any intermediate state. Simulations performed using a generalized tight-binding molecular dynamics method on 12% strained CNT also confirms the intermediate state and the corresponding pathway with a lowered activation energy. The small quantitative difference in the activation barriers, of the double-peak pathway, obtained with Tersoff-Brenner potential MD and quantum GTBMD methods are expected. The significant lowering of the activation barrier for SW bond rotation and the formation of a pentagon-heptagon pair, is expected to affect the

electronic (via the junction of nanotubes) and mechanistic (breaking strength) applications of carbon nanotubes.

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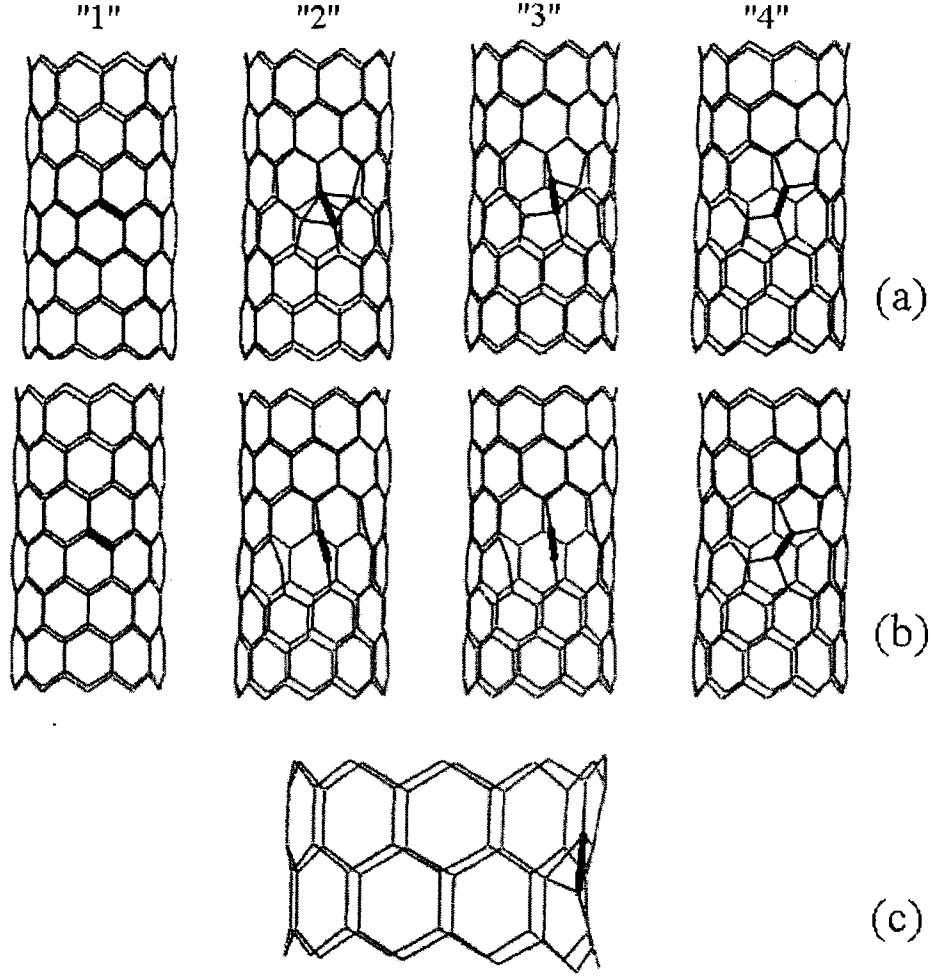


FIG. 1: (a) An activation process of Stone-Wales bond rotation during MD simulations on a 13.75% tensile strained (10,0) CNT at $T = 800\text{K}$. Four sequent configurations labeled as "1", "2", "3", and "4" respectively are shown. The configuration "2" shows an intermediate state with formation of sp^3 -like bonds during the activation process. (b) Same as (a), but with the direct in-plane bond rotation without any sp^3 -like bonding intermediate state. The rotated C-C bond is marked with dark black in both (a) and (b). (c) The close-up of the relaxed configuration of the sp^3 -like intermediate state in "2" of (a). The rotated C-C bond is marked in dark black and shows an off-plane tilting away from the CNT surface.

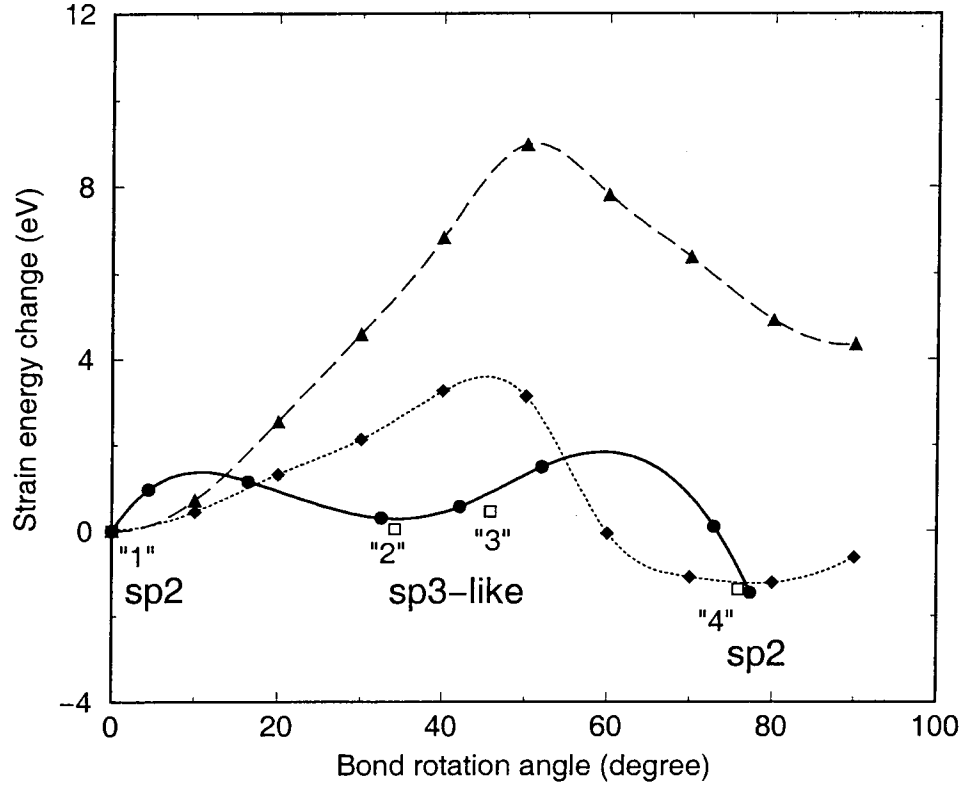


FIG. 2: The change in strain energy as a function of SW bond rotation angle. The solid line (spline curve) with circles is from the MD simulations on a 13.75% tensile strained CNT (10,0) at 800K. A saddle point with sp^3 -like configuration (shown in "2" of Fig. 1a) is observed. The cooled and quenched structures of "1", "2", "3", and "4" from Fig. 1a are marked as hollow squares. The long dashed line (spline curve) with triangles and the dotted line (spline curve) with diamonds are for the *static* process with direct in-plane rotation of the C-C bond on the CNT (10,0) at 0% and 13.75% tensile strain, respectively.

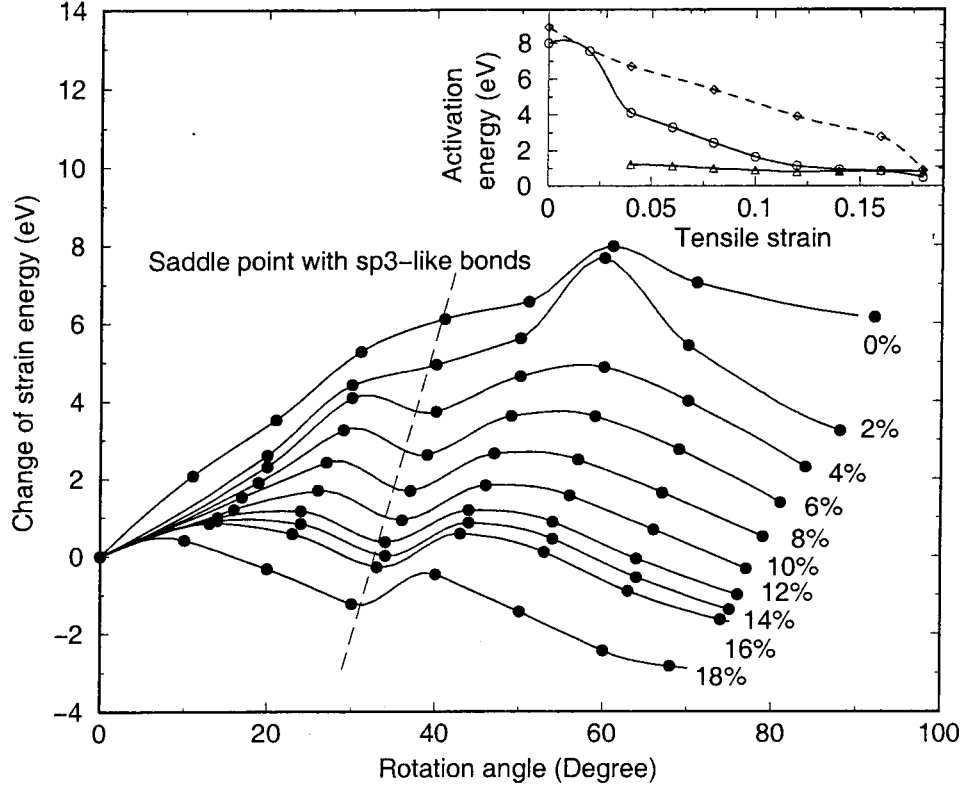


FIG. 3: The change in the energy of a tensile strained CNT (10,0) as a function of SW bond rotation angle, along the pathway with an intermediate state of sp^3 -like bonds. The tensile strain is varied from 0% to 18%, and the saddle point becomes locally stable to give a two-step activation process. Insert: The activation energy as a function of tensile strain on the CNT (10,0) for the intermediate state (circles and triangles) and direct in-plane rotation (dashed line with diamonds) pathways, respectively. The solid line with circles is for the activation energy of the first step barrier and the solid line with triangles is for the second step barrier.

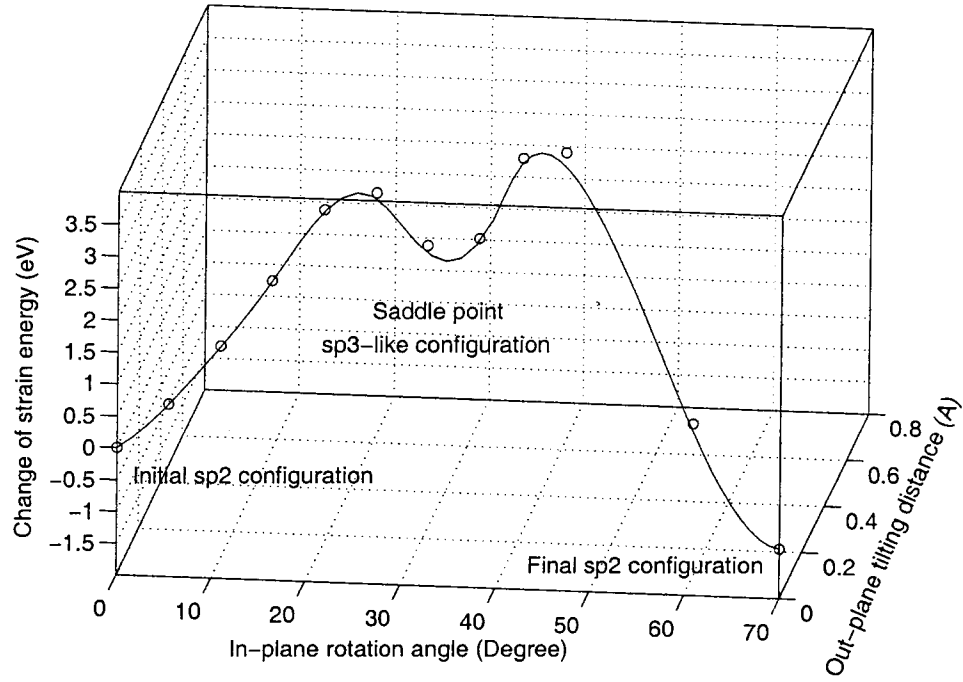


FIG. 4: The two-step activation barrier pathway searched using the generalized tight binding molecular dynamics method. The change of energy as a function of in-plane bond rotation angle and off-plane tilting distance for a 12% tensile strained CNT (10,0) is shown. The saddle point occurs at a rotation angle of about 30 degree and a tilting distance of about 0.7 Å.